

The Quinonoid Structure of Some Organic Compounds

A DISSERTATION

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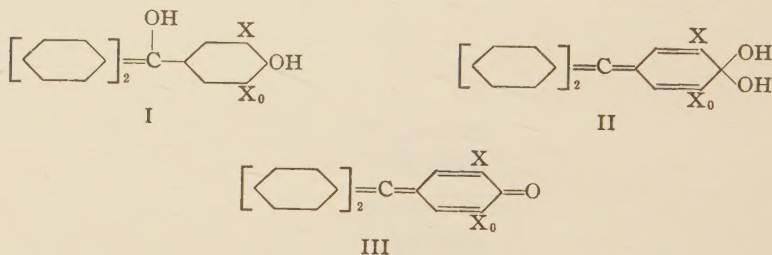
TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS. III

By LEIGH C. ANDERSON AND M. B. GEIGER¹

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Previous papers from this Laboratory² have shown that a marked change in absorption spectra occurs on changing from the colorless benzenoid *p*-hydroxytriphenylcarbinols to the corresponding colored carbinols. These spectroscopic data were interpreted as constituting further evidence for the existence of a quinonoid tautomer (II) of the corresponding benzenoid carbinol (I). The fact that the colorless carbinol possesses a benzenoid structure has not been doubted, and the structure of the corresponding fuchsone (III) has never been called in question. Explanations for the



existence of the colored carbinol, however, have implied the suggestion that it is a hydrate of the fuchsone,³ or that it is a mixture of the benzenoid carbinol with small amounts of the highly colored fuchsone as impurity. Chemical evidence by Gomberg and co-workers⁴ has definitely shown that the colored carbinol is not an impure benzenoid carbinol.

This work was undertaken in order to obtain further data concerning this class of compounds with the hope that certain effects that were observed in previous work in regard to the position and height of the absorption bands might now be explained.

¹ The material in this and the succeeding paper comprises a portion of a thesis presented by M. B. Geiger to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1931.

² (a) Anderson and Gomberg, *THIS JOURNAL*, 50, 203 (1928); (b) Anderson, *ibid.*, 51, 1889 (1929).

³ (a) Auwers and Schröter, *Ber.*, 36, 3247 (1903); (b) Orndorff, Gibbs, McNulty and Shapiro, *THIS JOURNAL*, 49, 1546 (1927). In the latter article the statement is made that "Gomberg has shown that fuchsone readily takes up water to form the quinoid hydrate." The word hydrate in this connection is ambiguous and was not used by Gomberg. He states in the article from which the above inference was drawn [*THIS JOURNAL*, 35, 1037 (1913)] "nor does either of the two molecules contain water of crystallization."

⁴ Gomberg, *THIS JOURNAL*, 35, 1035 (1913); Gomberg and Van Stone, *ibid.*, 38, 1577 (1916).

In Figs. 1, 2, 3 and 4, respectively, are given the curves for the quantitative spectra of the methane, colorless carbinol (except for the 3-chloro-), colored carbinol, and the fuchsons of each of the following: 3-chloro-4-hydroxy-, 3-bromo-4-hydroxy-, 3,5-dichloro-4-hydroxy- and 3,5-dibromo-4-hydroxytriphenylcarbinol. The methanes and colorless carbinols are undoubtedly benzenoid in constitution while the fuchsons contain a quinonoid nucleus.

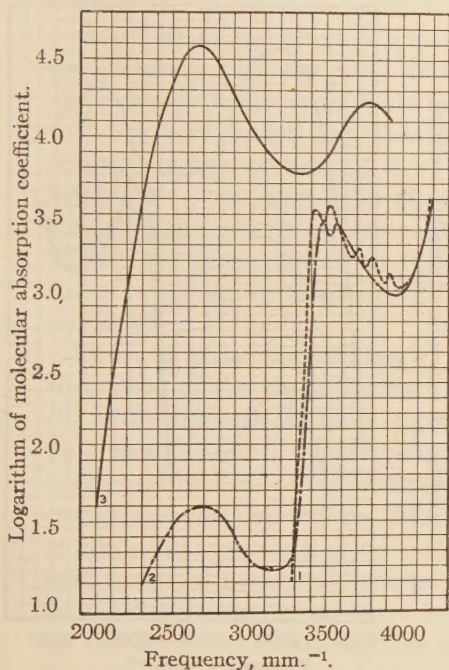


Fig. 1.—3-Chloro-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson. 4, carbinol, colorless.

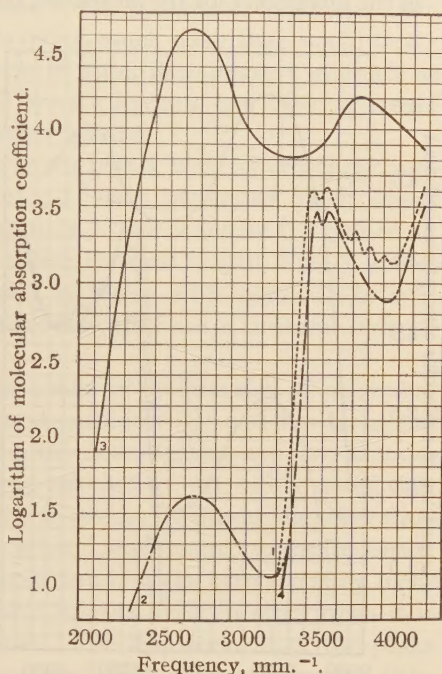


Fig. 2.—3-Bromo-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson; 4, carbinol, colorless.

The similarity of the curves for the corresponding derivatives in each of the groups is very striking. All of the fuchsons have an intense absorption band on the edge of the visible region of the spectrum and another band in the ultraviolet. The methanes have no absorption in the visible region but have a series of bands in the ultraviolet between frequencies 3400 and 4000 mm^{-1} . The benzenoid carbinols show no absorption in the visible region of the spectrum, and their ultraviolet absorption consists of a number of fine bands very similar to those of the methanes. The colored carbinols have spectra resembling both the fuchsons and the benzenoid carbinols in that they have an absorption band in the visible region of the spectrum and the ultraviolet absorption is practically identical with the ultraviolet absorption of the colorless carbinol.

The progressive substitution of one chlorine atom, one bromine atom, two chlorine atoms and two bromine atoms for the hydrogens in the ortho positions to the nuclear hydroxyl group in the 4-hydroxytriphenylcarbinol compounds causes a shift in the intense absorption band for the fuchsones toward the longer wave lengths. A similar change is noted for the band in the visible for the colored carbinols and for the two most persistent bands in the ultraviolet for the methanes, colorless carbinols and colored carbinols.

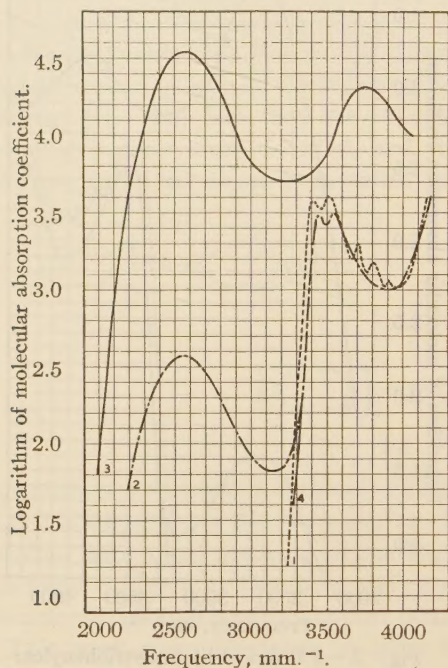


Fig. 3.—3,5-dichloro-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson; 4, carbinol, colorless.

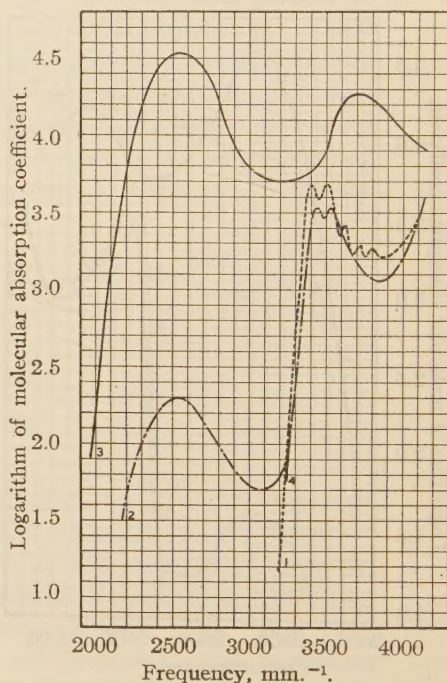


Fig. 4.—3,5-Dibromo-4-hydroxytriphenylcarbinol: 1, methane; 2, carbinol, colored; 3, fuchson; 4, carbinol, colorless.

The height of the quinonoid band⁵ for the various fuchsones is approximately the same. In all cases which have been observed the quinonoid band for the colored carbinols is much lower than the quinonoid band for the fuchsones; Table I lists the heights of the quinonoid bands of the fuchsones and the colored carbinols expressed as logarithms of the molecular absorption coefficients. If the colored carbinol were a hydrate of the corresponding fuchson such a variation would not be expected. The curve for the hydrate calculated on the basis of fuchson should be 93.5%

⁵ The band which occurs in the edge of the visible and near ultraviolet in the spectra of these fuchsones and colored carbinols will be called, for convenience of description, the quinonoid band.

TABLE I
HEIGHTS OF THE QUINONOID BANDS

3-X,5-X ₀ ,4-hydroxy- triphenylcarbinol	a		b		c		d		e	
	X H	X ₀ H	X H	X ₀ Cl	X H	X ₀ Br	X Cl	X ₀ Cl	X Br	X ₀ Br
Fuchsones	4.48		4.58		4.64		4.54		4.53	
Colored carbinols	2.52		1.59		1.61		2.57		2.30	

as high as the curve for the fuchsones. The difference which has been found in the height of the bands is, therefore, much more than would be accounted for by the effect of a molecule of water in so heavy a molecule as the fuchsones, even assuming that it were a hydrate and that it would all remain hydrated in so dilute an ether solution.

It has been found that the colored carbinols with symmetrical substitution in the nucleus (a, d, e, Table I) have quinonoid bands whose heights are of the same order of magnitude. The height of the quinonoid bands for the colored carbinols with unsymmetrical substitution (b and c, Table I) is even lower than the band for those with symmetrical substitution, but when compared with each other, they are of the same order of magnitude.

Figure 5 gives the position of the peaks or frequencies of maximum absorption of the bands for the colored carbinols (Q) and the fuchsones (F) of the different carbinols studied in this investigation and also includes those described in the papers previously referred to. It will be noted that in the case of some of the carbinols the frequency of maximum absorption of the quinonoid band for the colored carbinol as compared to the frequency of maximum absorption of the quinonoid band for the corresponding fuchsones is shifted toward the shorter wave lengths while in other cases it is shifted toward the longer wave lengths. The displacement of the peaks for the colored carbinols and the corresponding fuchsones is greater than the experimental error of determining the position of these peaks for the compounds indicated as a, c, d, f, g, h and i while for b and e the displacement is less than the experimental error. In a, h and i the peak for the fuchsones compared to that of the corresponding carbinol is displaced toward the shorter wave lengths, while in all the other groups the displacement is toward the longer wave lengths. These data allow an interesting observation to be made. When the groups in the ortho position to the nuclear hydroxyl are the same (a, h and i) the displacement of the peak for the quinonoid band of the colored carbinol compared to that of the fuchsones is toward the longer wave lengths. If the groups in the ortho position to the nuclear hydroxyl are not alike, then the displacement is in the opposite sense. It does not seem likely that this relation is due to chance, since no inconsistencies have been observed in any of the compounds studied.

The fact that the position of the quinonoid band for the colored carbinol and the quinonoid band for the corresponding fuchsones is not at the same

frequency is a positive indication that the colored carbinol is not the colorless carbinol with small amounts of fuchson as impurity. The two effects, namely, the displacement of the quinonoid band for the colored carbinol as compared to that of the fuchson and the lowering of the quinonoid absorption band of the colored form of 4-hydroxytriphenylcarbinol by a

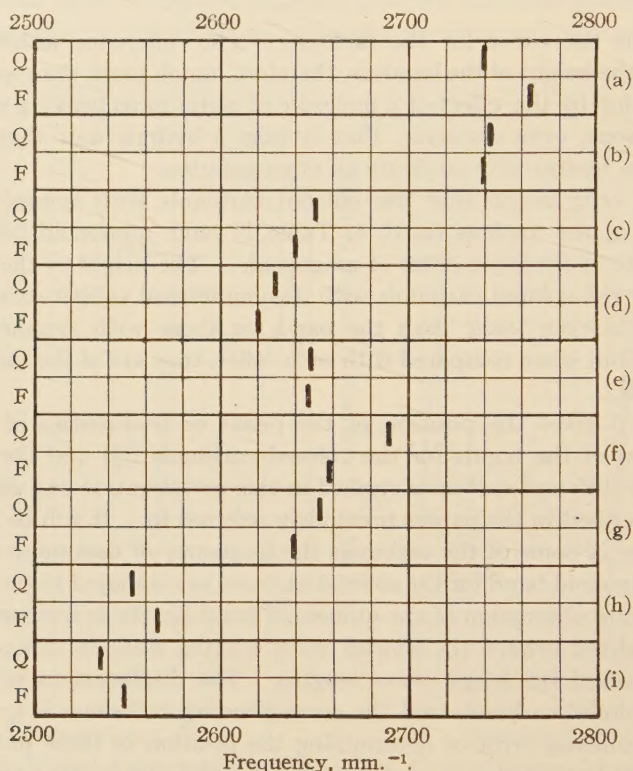


Fig. 5.—Q = colored carbinol; F = fuchson: (a) 4-hydroxytriphenylcarbinol; (b) 3-methyl-4-hydroxytriphenylcarbinol; (c) 3-methyl-5-chloro-4-hydroxytriphenylcarbinol; (d) 3-methyl-5-bromo-4-hydroxytriphenylcarbinol; (e) 3-methoxy-4-hydroxytriphenylcarbinol; (f) 3-chloro-4-hydroxytriphenylcarbinol; (g) 3-bromo-4-hydroxytriphenylcarbinol; (h) 3,5-dichloro-4-hydroxytriphenylcarbinol; (i) 3,5-dibromo-4-hydroxytriphenylcarbinol.

definite amount, both of which phenomena occur when one and two of the hydrogens adjacent to the nuclear hydroxyl group are replaced, appear to be evidence in favor of the hypothesis that the ring in which the substitution has been made has a very direct influence upon the nature of the electron transition which produces this band and also upon the probability of the occurrence of this transition.

TABLE II
 FREQUENCY NUMBERS OF BANDS IN ETHER SOLUTIONS

	3-Cl-4-OH triphenyl	3-Br-4-OH triphenyl	3,5-Cl ₂ -4-OH triphenyl	3,5-Br ₂ -4-OH triphenyl
Methane	3449	3433	3414	3409
	3530	3516	3508	3502
	3704	3702	3700	3702
	3802	3802	3802	3804
	3901	3906	3897	3906
	4014			
Carbinol (colorless)		3463	3445	3436
		3548	3550	3532
		3715	3654	3633
		3770	3717	3715
		3865	3771	3770
		3960	3865	3866
			3963	3963
Carbinol (colored)	2690	2654	2552	2540
	3477	3463	3445	3430
	3558	3549	3547	3520
	3720	3644	3658	3639
	3771	3718	3720	3715
	3862	3770	3783	3786
	3958	3859	3864	3865
		3949	3956	3956
Carbinol fuchsone	2659	2639	2567	2550
	3713	3720	3701	3668

Experimental

The apparatus and the methods used for obtaining the quantitative absorption spectra as well as the methods employed for determining the frequencies of maximum absorption have been described.²

The four fuchsones studied in this investigation were each prepared according to the method of Gomberg and Van Stone.⁴ They were all carefully crystallized from ether which showed no selective absorption between 2300 and 7500 Å. The four colored carbinols were prepared by adding hot water to a solution of the corresponding fuchsone in glacial acetic acid until the concentration of the acetic acid in the solution had been reduced to 60%. After allowing the mixture to cool the crystals were filtered off and dried in a vacuum desiccator over soda lime. Each of the three colorless carbinols was prepared by dissolving the corresponding fuchsone in normal alkali and treating the clear, cold solution with ammonium chloride. The precipitate was filtered off and crystallized from optically clear ether and hexane. The four methanes that were studied were prepared by reducing the corresponding fuchsone with zinc dust and glacial acetic acid. Each of them was crystallized from optically clear hexane. The melting points of the compounds prepared as described above are as follows (degrees centigrade):

	Methane	Colorless	Carbinol Colored	Fuchsone
3-Chloro-4-hydroxytriphenyl	73		124-125	161
3-Bromo-4-hydroxytriphenyl	79	108.5-109	105-105.5	139.5
3,5-Dichloro-4-hydroxytriphenyl	105	132	133-134	216
3,5-Dibromo-4-hydroxytriphenyl	130	136	136-137	233

Summary

1. Curves have been prepared which show the quantitative absorption spectra of the methane, colored carbinol and fuchsons of each of the following compounds: 3-chloro-4-hydroxytriphenylcarbinol, 3-bromo-4-hydroxytriphenylcarbinol, 3,5-dichloro-4-hydroxytriphenylcarbinol and 3,5-dibromo-4-hydroxytriphenylcarbinol together with the curves for the colorless carbinols of the last three compounds.

2. Symmetrical or unsymmetrical substitution in the ortho positions to the nuclear hydroxyl group of 4-hydroxytriphenylcarbinol has been shown to have a definite effect upon the height of the quinonoid band for the colored carbinol; symmetrical substitution producing a greater absorption.

3. The direction of the displacement of the quinonoid band for the colored carbinol, in reference to the position for the quinonoid band for the corresponding fuchsons of the 4-hydroxytriphenylcarbinol series has also been found to be dependent upon the groups substituted in the ortho positions to the nuclear hydroxyl. If the two groups are the same the displacement is in one direction, while if they are different, the displacement is in the opposite direction.

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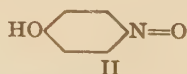
THE TAUTOMERISM OF QUINONEOXIME AND PARA-NITROSOPHENOL

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The chemical reactions and the methods of preparation of quinoneoxime (I) indicate that it is in tautomeric equilibrium with *p*-nitrosophenol (II); the relative amounts of the two substances present being dependent upon the solvent and conditions which are employed.



It has been generally accepted that the methyl ethers of tautomeric substances do not undergo tautomerization and that in many instances each can be obtained pure. A comparison of the physical properties of a solution of the tautomeric mixture of non-methylated substances with solutions of each of the corresponding methyl ether isomers has been used in investigations of compounds such as isatin, acetoacetic ester, etc., to determine the extent to which each of the tautomeric forms occurs in the equilibrium mixture. This procedure has been followed in the present investigation in the case of the mixture of quinoneoxime and *p*-nitrosophenol. Ether has been chosen as the solvent because it is optically

clear in the visible and ultraviolet regions, it is chemically inert toward solutes and also because all the compounds included in this work are monomolecular in this solvent. Sluiter¹ has shown that *p*-nitrosophenol, which is polymolecular in most solvents, is monomolecular in ether regardless of the concentration of the solution.

The methyl ethers of quinoneoxime (III) and of *p*-nitrosophenol (IV) have been described in the literature. A comparison of the quantita-



tive absorption spectrum of the tautomeric mixture of quinoneoxime and *p*-nitrosophenol with that of each of the ethers should indicate which form is present to the greater extent. These curves are presented in Fig. 1. The similarity in the curves for quinoneoxime methyl ether and the tautomeric mixture is obvious. The absorption curve for *p*-nitrosoanisole differs from the curves of the other solutions in that it shows no indication of fine bands in the edge of the visible region and the band in the ultra-violet is much narrower.

The similarity of the curves for the tautomeric mixture and quinoneoxime methyl ether leaves no doubt that the mixture in ether solution is mainly in the quinoneoxime form. On the assumption that the curves for pure quinoneoxime and pure *p*-nitrosophenol should be similar each to the curve for the corresponding methyl ether, it is possible from Fig. 1 to

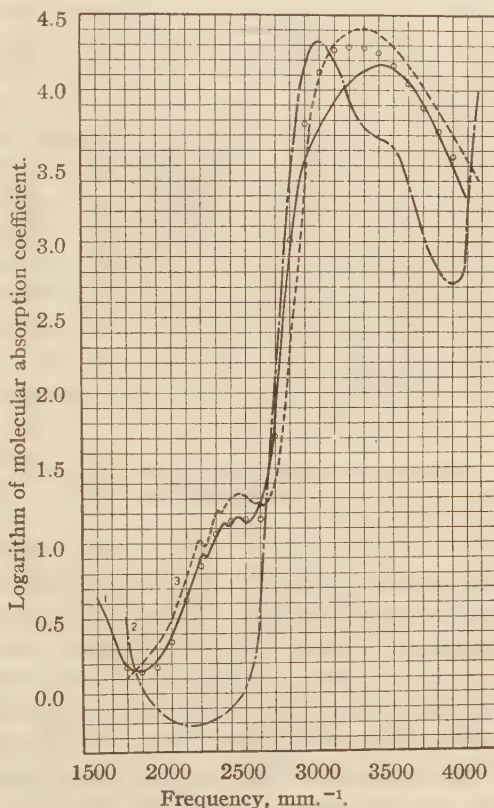


Fig. 1.—1, Tautomeric mixture of quinoneoxime and *p*-nitrosophenol; 2, *p*-nitrosoanisole; 3, quinoneoxime methyl ether.

make an estimate of the composition of the mixture. A comparison of the

¹ Sluiter, *Rec. trav. chim.*, **25**, 8 (1906).

quantitative absorption curves which are given in Fig. 2 for hydroquinone and its mono- and dimethyl ethers indicates that in these compounds the principal effect produced upon methylation is a displacement of the absorption toward the shorter wave lengths.

An examination of the curves in Fig. 1 shows that between frequencies 2000 and 2500 mm.^{-1} the *p*-nitrosophenol tautomer should have little influence on the height of the curve of the mixture; and since curve 1 is about 70% as high as curve 3 within this region, the mixture should contain approximately 70% quinoxneoime and 30% *p*-nitrosophenol. Using

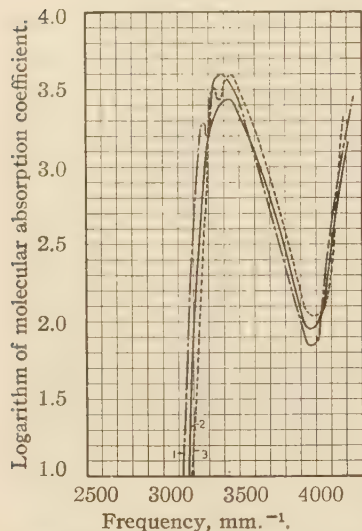


Fig. 2.—1, Hydroquinone; 2, hydroquinone monomethyl ether; 3, hydroquinone dimethyl ether.

values corresponding to such a mixture of methyl ethers and extending the calculations out to the regions where both compounds influence the absorption curve of the mixture, the values indicated by the circles in Fig. 1 are obtained. It will be seen that the agreement is very good except near the top of the absorption band in the ultraviolet. The disagreement within this region probably indicates that our assumption of the close similarity of the curves of the methyl ethers to the corresponding hydroxy compounds does not hold within these limits. Studies of solutions of this tautomeric mixture in other solvents are being carried on.

The curves for the quantitative absorption spectra for quinone, quinonechlorimine and quinonedichlorodiimine are shown in Fig. 3, and the curves for quinone and quinonedioxime are shown in Fig. 4.

In the latter figure a curve has been included for the absorption spectrum that we should expect to obtain from a sample of pure quinoneoxime. That portion of the curve has been omitted where the previously made assumptions do not seem to apply. The frequencies of maximum absorption for the bands in the visible which are indicated in Fig. 4 and in the table are the same as those found for quinoneoxime in the tautomeric mixture. The compounds in Fig. 3 are the derivatives of quinone in which the ketonic oxygen has been replaced by the $=\text{NCl}$ group, and the compounds in Fig. 4 are the derivatives of quinone in which the ketonic oxygen has been replaced by the $=\text{NOH}$ group.

The progressive changes which are noted on the successive substitution of the $=\text{NCl}$ group for a $=\text{O}$ group in quinone are the shifting of the ultraviolet band toward the visible and a shifting of the bands in the visible

region toward the ultraviolet. In quinonedichlorodiimine we find only one intense band. The ultraviolet band as we pass through the series successively persists over a greater dilution being least for quinone and greatest for quinonedichlorodiimine. In Fig. 4, similar changes are noted for the $=\text{NOH}$ compounds. The curves for quinonechlorimine and the calculated one for quinoneoxime are very similar to each other, as are also the curves for quinonedioxime and quinonedichlorodiimine.

The quantitative absorption curves for the reduction products of each: quinone, quinoneimine and quinonediimine, namely, the curves for hydroquinone, *p*-aminophenol and *p*-phenylenediamine, are given in Fig. 5.² The solvent used was absolute ether. *p*-Aminophenol and *p*-phenylenediamine may be considered as derived from hydroquinone by

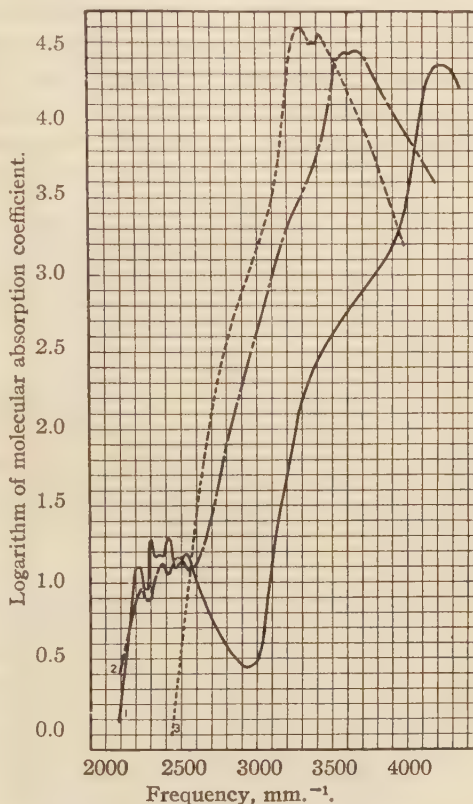


Fig. 3.—1, Quinone; 2, quinone chlorimine; 3, quinonedichlorodiimine.

FREQUENCY NUMBERS OF BANDS IN ETHER SOLUTIONS

Quinoneoxime.....	2095	2210	2349	2456	3417			
Quinoneoxime methyl ether....	2187	2301	2447	2575	3234			
<i>p</i> -Nitrosoanisole.....				2989	3493			
Hydroquinone.....				3270	3373			
Hydroquinone methyl ether....					3415			
Hydroquinone dimethyl ether...				3345	3436			
Quinone.....	2125	2200	2236	2317	2360	2429	3580	4123
Quinonedioxime.....					3212			
Quinonechlorimine.....	2155	2267	2380	3459	3557			
Quinonedichlorimine.....				3184	3260	3305		
<i>p</i> -Aminophenol.....				3228				
<i>p</i> -Phenylenediamine.....				3099				

² References to previous work upon the absorption spectra of quinone, its methyl ethers, hydroquinone, *p*-aminophenol and *p*-phenylenediamine may be found in Volume V of the "International Critical Tables."

the replacement of the hydroxyl groups of hydroquinone with amino groups. The regular changes in absorption curves which accompany these replacements are, first, a shifting of the absorption toward the visible region and, second, a decrease in its persistence.

The question of the structure of quinone and its derivatives has received considerable attention in the past. The assignment of the di-

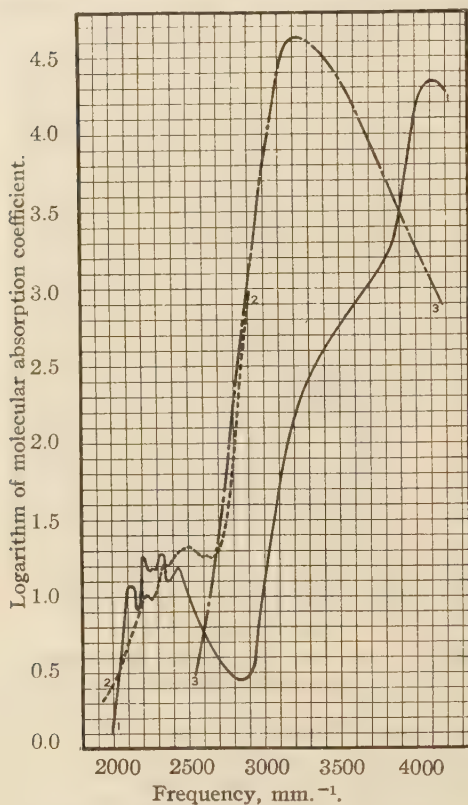


Fig. 4.—1, Quinone; 2, quinoneoxime (calcd.); 3, quinonedioxime.

ketic formula to quinone has been favored by evidence obtained by Garner and Sugden³ from parachor measurements, by Pascal⁴ from magnetic susceptibility measurements and by Light⁵ from absorption spectra data. The most recent data which favor the peroxidic formula were presented by Binder⁶ from heats of combustion. If the quinone derivatives are better represented by the peroxidic structure, then the general location and the height of the absorption bands of these derivatives should resemble those of hydroquinone and its derivatives, since under such an assumption, they would all contain a benzenoid nucleus. That there is, however, no such resemblance is evident from a comparison of the curves in Figs. 2 and 5 with those in Figs. 3 and 4. The compounds of known benzenoid structure of Figs. 2 and 5 have no absorption

in or adjacent to the visible region of the spectrum and the absorption band in the ultraviolet is only about one-tenth as persistent as the ultraviolet band for the quinone derivatives. Our conclusion, therefore, is that the diketonic structure best explains the data obtained from the absorption spectra.

³ Garner and Sugden, *J. Chem. Soc.*, 2877 (1927).

⁴ Pascal, *Bull. soc. chim.*, [4] 9, 339, 812 (1911).

⁵ Light, *Z. physik. Chem.*, 122, 414 (1926).

⁶ Binder, *Chem.-Ztg.*, 45, 1114 (1921).

Experimental

The instruments and methods used for obtaining the quantitative absorption curves and points of maximum absorption have been described.⁷ In the purification of all the compounds except quinone, *p*-aminophenol and *p*-phenylenediamine the final recrystallization was carried out from a solvent which showed no selective absorption between 2300 and 7500 Å. The material which on solution in ether produced the tautomeric mixture of quinoneoxime and *p*-nitrosophenol was prepared by the action of nitrous acid on phenol. The product was first crystallized from water using charcoal for decolorizing, and finally from ether; m. p. 128–129°.

***p*-Nitrosoanisole.**—*p*-Nitrosoanisole was reduced to the corresponding hydroxylamine and this compound was oxidized to the nitroso derivative by the method described by Rising.⁸ The product was purified by distillation with steam and was crystallized from hexane; m. p. 22.5°.

Quinoneoxime methyl ether was obtained by the methylation of quinoneoxime with diazomethane.⁹ It was crystallized from hexane; m. p. 82°.

***p*-Quinone** was prepared by the oxidation of hydroquinone with chromic acid. The crude product was purified by several successive sublimations; m. p. 116°.

Quinonechlorimine was obtained by the action of sodium hypochlorite on the hydrochloride of *p*-aminophenol.¹⁰ The material was crystallized from hexane; m. p. 87°.

Quinonedichlorodiimine resulted from the oxidation of *p*-phenylenediamine hydrochloride with sodium hypochlorite.¹⁰ The product was crystallized from hexane; m. p. 128° with decomposition.

Quinonedioxime was prepared by the action of hydroxylamine hydrochloride on quinoneoxime.¹¹ The material was crystallized from ether; m. p. 242° with decomposition.

Hydroquinone.—Kahlbaum's product was crystallized from water using charcoal for decolorizing; m. p. 169°.

Kahlbaum hydroquinone monomethyl ether was crystallized from hexane; m. p. 55.5°.

The dimethyl ether of hydroquinone was obtained by crystallizing an Eastman product from 95% alcohol; m. p. 56°.

Eastman *p*-aminophenol was purified by sublimation at 180° under reduced pressure (2 mm.); m. p. 184° with decomposition.

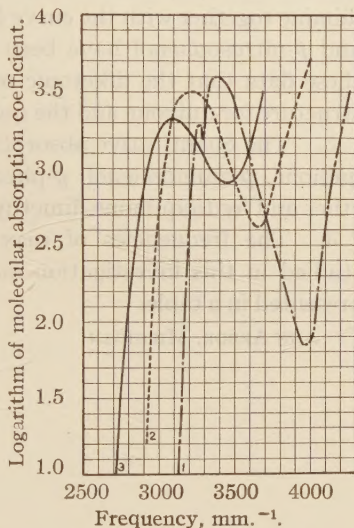


Fig. 5.—1, Hydroquinone; 2, *p*-aminophenol; 3, *p*-phenylenediamine.

⁷ Anderson and Gomberg, *THIS JOURNAL*, **50**, 203 (1928); Anderson, *ibid.*, **51**, 1889 (1929).

⁸ Rising, *Ber.*, **37**, 44 (1904).

⁹ Von Pechmann and Seel, *ibid.*, **31**, 299 (1898).

¹⁰ Willstätter and Mayer, *ibid.*, **37**, 1498 (1904).

¹¹ Lobry de Bruyn, *Rec. trav. chim.*, **13**, 109 (1894).

Eastman's *p*-phenylenediamine was sublimed at 200° under reduced pressure (2 mm.); the pure white product melted at 140°.

Summary

1. The quantitative absorption curves for ether solutions of *p*-nitrosoanisole, the methyl ether of quinoneoxime and of quinoneoxime have been determined. The spectroscopic results indicate that quinoneoxime and *p*-nitrosophenol are in tautomeric equilibrium in ether solutions in the ratio of approximately seven parts of the former to three parts of the latter.

2. The quantitative absorption spectra of ether solutions of quinone, quinoneoxime, quinonedioxime, quinonechlorimine and quinonedichlorodiimine together with the curve for the tautomeric mixture of quinoneoxime, and *p*-nitrosophenol have been obtained. The conclusion is drawn from these data that the diketonc or quinonoid formula represents the correct structure for quinone and the quinone derivatives.

3. The quantitative absorption curves for the ether solutions of hydroquinone, *p*-aminophenol, *p*-phenylenediamine, hydroquinone monomethyl ether and hydroquinone dimethyl ether have been obtained.

4. The frequencies of maximum absorption for all the compounds studied in this investigation have been ascertained and these values are presented in a table.

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